

Characterization of Heavy Metal Incorporation in Calcite by XAFS Spectroscopy	X11A
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Coprecipitation is one of the environmentally important processes governing the distribution and fate of dissolved heavy metals in near-surface waters. Recently reported experimental work on the coprecipitation of divalent Co, Zn, Mn, Fe, Cd, Sr, Pb, and Ba with calcite (a common authigenic phase in soils and aquifer materials) has shown strongly selective uptake in structurally distinct surface sites on the calcite 1014 face, resulting in element-specific, differential incorporation during crystal growth. XAFS spectra of individual divalent heavy metals (Co, Zn, Pb, and Ba) coprecipitated with calcite were collected (X11A) and analyzed to determine local coordination in the bulk following surface-controlled differential uptake. Results of multi-shell fitting using FEFF6 and FEFFIT show that, despite their large difference in size, all four metals attain a coordination with six oxygens at distances that are consistent with octahedral coordination. Substitution of the metal ions therefore occurs in the Ca site, which is confirmed by second-shell distances. One conclusion is that despite distinct surface-site preferences and uptake patterns varying in magnitude by more than a factor of ten, bulk coordination differs only minimally. Therefore, differential surface uptake need not result in different coordination in the bulk calcite as heavy metal ions are buried during growth. A further conclusion is that relaxation around an impurity ion is very localized, and the corner-sharing structural topology of calcite facilitates the observed wide spectrum of impurity substitution.